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(54) **Title**: A REFERENCE ELECTRODE AND A METHOD THEREOF

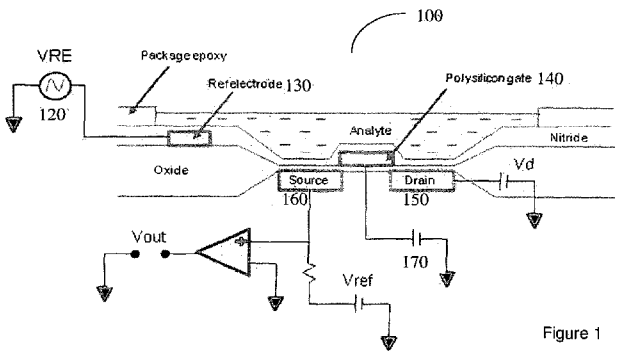


Figure 1

(57) **Abstract**: A reference electrode (130) for sensing pH is provided in an ambient electrolyte solution in an ion sensitive field effect transistor (ISFET) (100) which includes a source (160), a drain (150) and a gate (140), characterized in that, the reference electrode (130) includes an alternating current source, an insulating membrane separating the reference electrode (130) from the ambient electrolyte solution, a direct current (DC) biasing voltage (170) at the gate (140) wherein the voltage is a predetermined constant voltage, wherein the reference electrode (130) is connectable to the alternating current source (120) where the reference electrode (130) is further included in the gate (140) and the reference electrode (130) is constructed from Complementary metal-oxide-semiconductor (CMOS) compatible metal.

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A REFERENCE ELECTRODE AND A METHOD THEREOF

FIELD OF INVENTION

The present invention relates to a reference electrode to be used in an Ion Sensitive Field Effect Transistor (ISFET) sensor and a method thereof.

BACKGROUND OF INVENTION

ISFET or Ion Sensitive Field Effect Transistor is a silicon based device which is used to detect and measure presence of enzymes, pH, glucose, chemicals, soil nutrients and known with different names such as CHEMFET for chemical FET and ENFET for enzyme FET depending on applications. It has a fast response, robust and easily miniaturized through CMOS fabrication process. Similar to FET, it needs biasing at drain and source.

Tremendous improvement has been made on ISFET performance and reliability through better sensing materials and better packaging. However not much can be said of reference electrode. Solid state reference electrode has not been reliable while liquid junction base are bulky, costly and requires regular maintenance. Glass electrodes are predominantly used with ISFETs. However, these glass electrodes are bulky and costly as well as require maintenance such as replenishing with reference solution.

Apart from that, solid state reference electrodes which a less expensive and smaller than glass reference electrodes are found to be unstable when in direct contact with electrolyte and tend to corrode over time.

This makes it unattractive for applications such as Precision Agriculture (PA) where sensors are connected wirelessly through Wireless Sensor Network (WSN) and left in the field on their own. Applications such as these require robust, low cost and low power sensor where hundreds or thousands of sensors will be deployed.

U.S. 4,488,556 describes a CHEMFET device with a gate membrane coupled to monitored substance to maintain a fixed a voltage. However, the described device requires the reference electrode to be DC biased and this translates to having the reference electrode exposed to electrolyte, which will wear out over time and requires high maintenance.

Therefore there is a need for robust, low cost and low power sensors to be deployed in the field without having to maintain the sensors frequently by changing the reference electrodes. There is also a need for a method of use where reference electrodes are able to be used efficiently without DC biasing the reference electrodes.

SUMMARY OF INVENTION

Accordingly there is provided a reference electrode for sensing pH in an ambient electrolyte solution in an ion sensitive field effect transistor (ISFET) which includes a source, a drain and a gate, characterized in that, the reference electrode includes an alternating current source, an insulating membrane separating the reference electrode from the ambient electrolyte solution, a direct current (DC) biasing voltage at the gate wherein the voltage is a predetermined constant voltage, wherein the reference electrode is connectable to the alternating current source where the reference electrode is further included in the gate and the reference electrode is constructed from Complementary metal–oxide–semiconductor (CMOS) compatible metal.

There is also provided a method of pH sensing by a reference electrode in an ambient electrolyte solution in an ion sensitive field effect transistor (ISFET)which includes a source, a drain and a gate, characterized in that, the method includes the steps of providing a potential difference for a plurality of hydrogen ions to migrate to a reference surface of a reference electrode, modulating a conduction channel using an Amplitude Modulation (AM) signal to form a stable voltage across the drain to source of the ISFET, measuring the voltage to determine pH value of the electrolyte solution.

The present invention consists of several novel features and a combination of parts hereinafter fully described and illustrated in the accompanying description and drawings, it being understood that various changes in the details may be made without departing from the scope of the invention or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be fully understood from the detailed description given herein below and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention, wherein:

Figure 1 illustrates a circuit diagram of a reference electrode and an Ion Sensitive Field Effect Transistor (ISFET) in a preferred embodiment of the invention with an alternating current (AC) modulating signal; and

Figure 2 illustrates a voltage response of 5 different pH levels at different frequencies by using tungsten as a reference electrode.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention relates to a reference electrode to be used in an ISFET sensor and a method thereof. Hereinafter, this specification will describe the present invention according to the preferred embodiment of the present invention. However, it is to be understood that limiting the description to the preferred embodiment of the invention is merely to facilitate discussion of the present invention and it is envisioned that those skilled in the art may devise various modifications and equivalents without departing from the scope of the appended claims.

The following detailed description of the preferred embodiment will now be described in accordance with the attached drawings, either individually or in combination.

A preferred embodiment of the present invention as shown in Figure 1 provides for a reference electrode (130) for sensing pH in an ambient electrolyte solution in an ion sensitive field effect transistor (ISFET) (100) which includes a source (160), a drain (150) and a gate (140). The reference electrode (130) includes an insulating membrane separating the reference electrode (130) from the ambient electrolyte solution. The ISFET (100) gate (140), or polysilicon, further includes the reference electrode (130), the ambient electrolyte solution, such as an analyte and an insulating membrane separating the reference electrode (130) from the ambient electrolyte solution. The reference electrode (130) is constructed from Complementary metal–oxide–semiconductor (CMOS) compatible metal. The insulating membrane also functions as a pH sensing membrane and is constructed using a nitride membrane such as a silicone nitride (Si_3N_4) membrane. The silicon nitride membrane in this embodiment is of a thickness from 10 nanometers to 1.5 micrometers. It is to be appreciated that other

materials may be used for this purpose. A plurality of other sensing layers may also be added on top of the nitride membrane to detect other materials.

As with any other field effect transistor FET, biasing needs to be done at drain and source. A direct current (DC) biasing voltage (170) is supplied at the gate (140) wherein the voltage is a predetermined constant voltage. For example, the voltage used in this embodiment is 0 to 3 Volts (V). However, example given here is not limitative as the voltage may be determined based on application of the invention.

The reference electrode (130) is connectable to an alternating current (AC) source (120) which is an Amplitude Modulation (AM) signal at a relatively higher frequency modulated by a carrier frequency at a relatively lower frequency. An example of a lower frequency is from 1 Hertz (Hz) to 0.9 Mega Hertz (MHz) and an example of a higher frequency are from 1 MHz to 1 GHz. It is to be appreciated that the lower frequencies and higher frequencies are to be determined by application of the invention.

A method of pH sensing by a reference electrode (130) in an ambient electrolyte solution in an ion sensitive field effect transistor (ISFET) (100) which includes a source (160), a drain (150) and a gate (140) is described. A potential difference for a plurality of hydrogen ions to migrate to a reference surface of a reference electrode (130) is provided. A conduction channel using an Amplitude Modulation (AM) signal to form a stable voltage across the drain (150) to source (160) of the ISFET (100) is modulated and the voltage is then measured to determine pH value of the electrolyte solution. A logarithmic value of hydrogen ion concentrations is taken to be a pH value of the electrolyte and is directly reflected by the measured voltage.

Rather then using known methods of only DC biasing, the reference electrode is AC biased at frequencies typical of ions to be detected, such as but not restricted to, 1 kHz, 500 Hz, 100 Hz, 50 Hz and 10 Hz. Typically, any reference electrode biased with a DC voltage will be blocked by an insulating membrane. However, an AC signal is able to penetrate the insulating membrane. Hydrogen ions that are being used for pH detection can respond to a predetermined frequency, such as 10 Hz to 1 kilohertz (kHz) of AC signal. This makes direct AC biasing impossible as impedance of the insulating membrane will be too high to penetrate. As detected pH values vary with voltage amplitude of the reference electrode (130), an Amplitude Modulation (AM) signal at a relatively higher frequency, such as 1 MHz to 1 GHz is modulated by a carrier frequency at a lower frequency such as, 1 Hz to 0.9 MHz in order to penetrate the insulating membrane and modulate the conduction channel of ISFET for pH detection.

Existing technology uses glass and solid state reference electrode. However, this has been changed to a metal based reference electrode with an insulating membrane in order to protect the reference electrode (130) from corrosion due to electrolyte.

An example of an ISFET (100) pH sensor using an AM signal modulated reference electrode (130) is shown in Figure 2. For a stable output signal, a DC biasing voltage (170) can be established by biasing the gate (140) which is a polysilicon gate at a predetermined constant voltage, such as 0 to 3 V as seen in Figure 1. Further embodiments of the ISFET (100) pH sensor can be constructed using enhancement mode ISFET and depletion mode ISFET. When the reference electrode (130) is biased with the AM signal, the hydrogen ions respond to the AM signal and in turn modulate the drain (150) current, I_d.

Further, since the hydrogen ions have different mass and charge affinity, scanning frequencies that are received as output can help to identify exact ion species as each ion responds to a unique frequency. The reference electrode (130) together with the ISFET (100) is therefore able to function as a spectrometer.

Using this method, any metal can be used as a reference electrode (130) as long as it is separated from the electrolyte by an insulating membrane. Therefore, the reference electrode (130) and the ISFET (100) are fully integratable with CMOS processes where typical metals such as aluminium and tungsten may be insulated by a nitride membrane. Fabrication process is simplified and miniaturization of process and apparatus is easily implemented. Operation of the reference electrode (130) and the ISFET (100) as a pH sensor is simplified and is maintenance free.

It is to be understood that the embodiments of the invention described are exchangeable for other variations of the same in order to be used in various applications. The present embodiment of the invention is intended for, but not restricted to, for use in applications such as detecting and measuring presence of enzymes, glucose, chemicals and soil nutrients.

CLAIMS

1. A reference electrode (130) for sensing pH in an ambient electrolyte solution in an ion sensitive field effect transistor (ISFET) (100) which includes a source (160), a drain (150) and a gate (140), characterized in that, the reference electrode (130) includes:
    i. an alternating current source;
    ii. an insulating membrane separating the reference electrode (130) from the ambient electrolyte solution;
    iii. a direct current (DC) biasing voltage (170) at the gate (140) wherein the voltage is a predetermined constant voltage;

    wherein the reference electrode (130) is connectable to the alternating current source (120) where the reference electrode (130) is further included in the gate (140) and the reference electrode (130) is constructed from Complementary metal–oxide–semiconductor (CMOS) compatible metal.

2. The electrode (130) as claimed in claim 1, wherein the alternating current source (120) is an amplitude modulation (AM) signal at a high frequency modulated by a carrier frequency at a relatively lower frequency.

3. The electrode (130) as claimed in claim 1, wherein the insulating membrane is a nitride membrane such as a silicone nitride membrane.

4. The electrode (130) as claimed in claim 3, wherein a plurality of other sensing layers are added on top of the nitride membrane.

5. A method of pH sensing by a reference electrode (130) in an ambient electrolyte solution in an ion sensitive field effect transistor (ISFET) (100) which

includes a source (160), a drain (150) and a gate (140), characterized in that, the method includes the steps of:

i. providing a potential difference for a plurality of hydrogen ions to migrate to a *reference surface of a reference electrode* (130);

ii. modulating a conduction channel using an Amplitude Modulation (AM) signal to form a stable voltage across the drain (150) to source (160) of the ISFET (100);

iii. measuring the voltage to determine pH value of the electrolyte solution.

6. The electrode (130) and method as claimed in claim 1 and claim 5, wherein the electrode (130) and method are used to detect and measure presence of pH, enzymes, glucose, chemicals and soil nutrients.

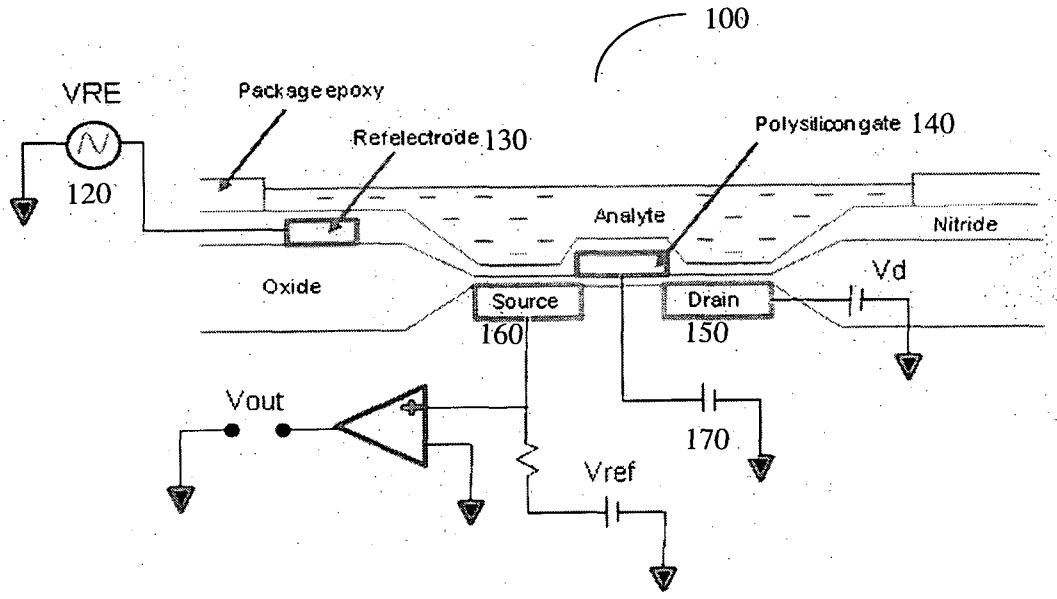


Figure 1

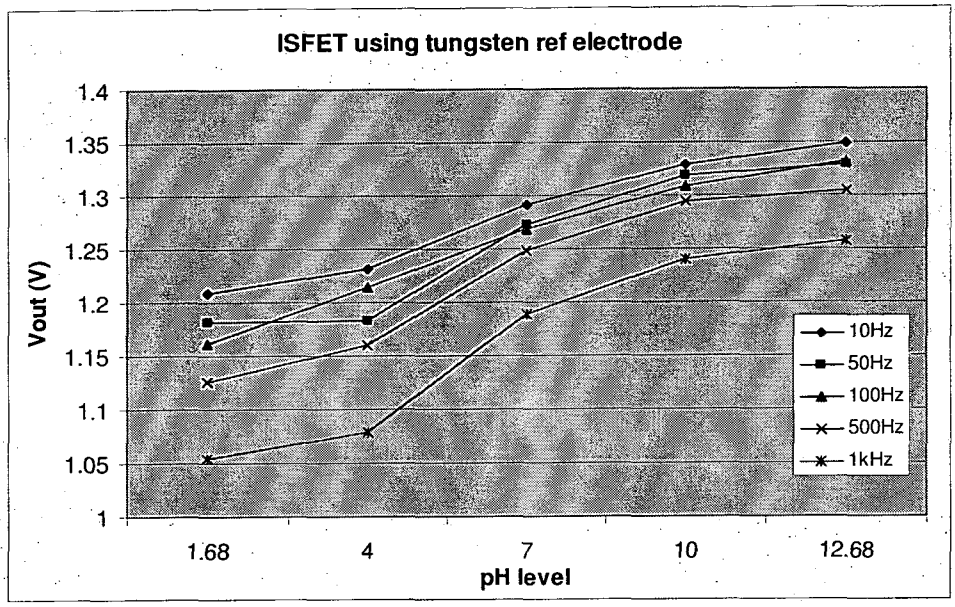


Figure 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2010/000175

A. CLASSIFICATION OF SUBJECT MATTER

G01N 27/414(2006.01)i, G01N 27/333(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N 27/414; G01N 27/00; C12Q 1/00; G01N 27/30; G01N 27/26; G01N 27/46; C12M 1/34

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: chemFET, ISFET, alternating current, amplitude modulation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 61-181951 A (SEITAI KINOU RIYOU KAGAKUHIN SHINSEIZOU GIJUTSU KENKYU KUMIA I et al.) 14 August 1986 see page 2; figs. 1-2.	1-6
A	US 2005-0230245 A1 (ARKADIY MORGENSHTEIN et al.) 20 October 2005 see page 7; figs. 5-6.	1-6
A	US 4488556 A1 (HO NELSON) 18 December 1984 see the abstract; column 4; fig. 4.	1-6
A	US 2003-0073071 A1 (JURGEN FRITZ et al.) 17 April 2003 see page 3; fig. 4.	1-6
A	Sensors and Actuators Vol.18, 119-129 (R.B.M. Schasfoort et al.) 15 June 1989 Influence of an immunological precipitate on D.C. and A.C. behaviour of an isfet see pages 119,123; fig. 3.	1-6

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
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"E" earlier application or patent but published on or after the international filing date
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Date of the actual completion of the international search	Date of mailing of the international search report
15 MARCH 2011 (15.03.2011)	**17 MARCH 2011 (17.03.2011)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/MY2010/000175

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 61-181951 A	14.08.1986	None	
US 2005-0230245 A1	20.10.2005	US 2009-294653 A1 US 7544979 B2 US 7799205 B2	03.12.2009 09.06.2009 21.09.2010
US 4488556 A1	18.12.1984	None	
US 2003-0073071 A1	17.04.2003	US 2008-0124717 A1	29.05.2008